

SBIR N03-120

New Low Cost Resin Systems

Applied Poleramic, Inc.

Final Report

Report Documentation Page				Form Approved OMB No. 0704-0188		
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.						
1. REPORT DATE 25 FEB 2004		2. REPORT TYPE Final		3. DATES COVERED 25 Jun 2003 - 25 Feb 2004		
4. TITLE AND SUBTITLE New Low Cost Resin Systems				5a. CONTRACT NUMBER N00014-03-M-0304		
				5b. GRANT NUMBER		
				5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Brian S. Hayes; Doyle Dixon				5d. PROJECT NUMBER		
				5e. TASK NUMBER		
				5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Applied Poleramic, Inc. 6166 Egret Court Benicia, CA 94510				8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)		
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT API has found that with the use of phosphorous containing compounds, used in the textile industry, substantial reduction in FST properties can be realized for VaRTM resins systems without loss in mechanical and physical properties. With using this new technology, API was able to develop an epoxy based resin system that exceeds the present state of art epoxy VaRTM resin formulations. Collectively, as stated in the objective of this SBIR, API was able to develop a VaRTM process able resin that had equal cone calorimeter results as Derakane 510-A, but had at least a 65% lower smoke value.						
15. SUBJECT TERMS						
16. SECURITY CLASSIFICATION OF:				17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 6	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified				

Introduction

It has been identified that the use of polymeric composite materials in submarine and ship construction can offer many advantages over that of steel structures. The utilization of these heterogeneous materials provides design and performance advantages that cannot be observed using homogenous metallic materials. Some of these advantages include lower weight structures due to anisotropic material properties, reduced corrosion arising from the polymeric matrix, and excellent fatigue life. In addition to these inherent composite characteristics, reduced dielectric and magnetic properties can also be realized. While these benefits are substantial, the negative aspect of fire, smoke, and toxicity (FST) of the organic matrices used in fiber reinforced composites has limited widespread utilization.

Future composite applications for Navy submarines and surface ships requires advanced polymeric matrices that have improved fire, smoke, and toxicity (FST) as compared to the present state of the art composite matrix resins of today. These matrix characteristics, along with the requirement of low cost composite manufacturing, provides a challenge for new resin development. As a first step in the development of matrix resins that meet the goal of Navy FST, is to develop a non-halogenated resin that is capable of vacuum assisted resin transfer molding (VARTM), and has the same or better FST performance when compared to Derakane 510A, a halogenated vinyl ester resin.

To develop matrix resins with improved FST characteristics, and capable of VARTM processing, new approaches were taken in parallel with new materials and formulations. API focused primarily on epoxy chemistry and modified these systems using a combination of reactive phosphorous and silicone compounds. A series of VARTM resins were developed and contained different reactive phosphorous and silicone/siloxane based modifiers. Through this research, API down-selected the best performing resins and further increased the FST performance to a level that has not been approached by epoxy resins, capable of VARTM and room temperature cure.

Research

Initial work by API focused on making new epoxy-phosphorous based adducts and qualitatively testing the FST characteristics using a simple Bunsen Burner Test. The phosphorous materials used to make the adducts were phenyl phosphonic acid (dihydroxyl) and benzene phosphinic acid (monohydroxyl functional). The dihydroxyl containing phosphorous compound was adducted with two different types of epoxy resins that included both low viscosity resorcinol diglycidyl ether (RDGE) and diglycidyl ether of bisphenol-A (DGEBA). 30 % of the epoxy groups of RDGE were reacted with the dihydroxyl acid and resulted 3.2 wt% phosphorous and a new epoxide equivalent weight of 207. Adducts were also made with DGEBA and the dihydroxyl phosphorous based acid but resulted in a substantial increased viscosity and therefore was not further investigated. Benzene phosphinic acid, monofunctional hydroxyl functional, was reacted with N, N, N', N'-tetraglycidylmethoxy diamine. For this adducted, 15 % of the epoxy groups were converted on N, N, N', N'-tetraglycidylmethoxy diamine corresponding to

3.67 % phosphorous and a new EEW of 148. The final formulations contained between 2.5 and 4 wt% phosphorous and were cured with m-xylenediamine (MXDA). In addition to phosphorous adducts that API developed, Silicone Solutions was subcontracted to synthesize a proprietary low viscosity silicone based compound that was co-reacted with standard epoxy and also reacted with amine functionality. A blend (50/50) of bisphenol-A and bisphenol-F epoxy was sent to Silicone Solutions for modification. Silicone Solutions modified the resin with 10 wt% silicone for curing into plaques by API. Resins were also tested having commercially available amine modified polysiloxane and an amino-functional silane. Epoxy resins were cured with MXDA at room temperature and then a postcure of 100C. All phosphorous based materials that were developed significantly reduced flammability of epoxy resins and was very noticeable when greater than 2.0 percent total phosphorous was added to the resin. However, there was no qualitative difference in burning or smoke when silicone or siloxane was used in the resins. One issue observed with all of the adducted phosphorous resins was that the cure speed increased to a level to high for VARTM.

API also worked on the development of synthesizing new phosphorous based epoxy resins for use as modifiers in the VARTM resins. The epoxy resin that was developed was bis(glycidyloxy) phenyl phosphine oxide. The theoretical molecular weight was 270 which corresponded to an epoxide equivalent weight (EEW) of 135. This was a low viscosity liquid of approximately 500 cps, but had difficulty developing a high level of purity. Even when diluted 70 wt% with a standard DGEBA resin, this material accelerated the epoxy reaction too much to make a VaRTM processable resin.

Due to the processing concerns associated with the new technology and the corresponding low improvements in the qualitative FST, API investigated other methods of reducing FST while also being VARTM processable. Materials used for modifying polymers in the textile industry for lowering FST were found to provide excellent improvements in epoxy resins and also not effect the processing of these resins.

Based on the new technology, API developed VaRTM capable resins using the newly developed technology for use in impregnating woven glass roving. These panels were made according to ASTM E1354 and tested using the Cone Calorimeter Test. A series of eight VaRTM resins were developed based on the newly developed phosphorous and silicon containing compound technology (Table 1).

Table 1. VARTM Resin Formulations

Resin Formulation	1	2	3	4	5	6	7	8
Epoxy DGEBA	50	50	50	50	54	60		
Epoxy DGA	40	40	40	40	40			
Epoxy DGEBF						30		
Epoxy-Silicone							90	90
Epoxy func. phosphorous compound	10		10			10	10	
Hydroxyl func. phosphorous compound		10						10

Triphenylphosphate					6			
Aminofunctional silane	1		1					1
Antimonytrihydrate	10	10	10	10	10	10	10	10
Melamine formaldehyde			10					
MXDA	24	22	24	20		20	20	18
Amine modified polysiloxane					43			
Phosphorous modified aromatic amine				10				

DGEBA-diglycidyl ether of bisphenol-A

DGA-diglycidyl aniline

DGEBF-diglycidyl ether of bisphenol-F

Epoxy silicone-Difunctional epoxy modified with reactive silicone from Silicone Solutions

MXDA-metaxylenediamine

All resins also contained a small quantity of sub-micron size antimony trihydrate, ATH, since it has been seen beneficial in past research. As seen in Table 1, resins 1-4 consisted of the same base epoxy resin. The difference between resins 1 and 2 was the type of phosphorous containing compound, where resin 3 was the same as resin 1 with the addition of melamine formaldehyde. Resin 4 contained a phosphorous containing aromatic amine as part of the curing agent. Resin number 5 contained a similar base epoxy and had a different phosphorous materials, triphenyl phosphate (TPP), and was cured with a reactive polysiloxane. Different from resins 1-4, the phosphorus is not reactive in the formulation. Resin number 6 was developed to observe the difference in base epoxy when compared to resin number 1. Resin number 7 and 8 were developed with a pre-adducted silicone to a based epoxy resin. This material was developed by Silicone Solutions through a sub-contract with API. These two resins compared the effect of the two phosphorous modifiers and the effect of the novel reacted silicone in the formulations. These eight VaRTM resins were developed to understand fundamental differences in components in the formulations for down selection of the final formulation. Testing was performed at VTEC labs, using ASTM E1354-Cone Calorimeter Testing. All specimens had a thickness of 5.2 mm and were subjected to a heat flux of 50 kW. Results are summarized in the Table 2.

Table 2. Results of Cone Calorimeter Testing of VARTM Resins

Resin #	1	2	3	4	5	6	7	8
Time to Ignition (s)	123	114	111	82	121	119	121	133
Peak HRR (KW/sq. m)	226.35	201.85	194.59	174.44	201.13	173.48	193.80	194.32
Avg. HRR During Burning	89.52	99.12	91.06	83.08	114.38	87.95	100.86	96.70
Avg. HRR (180 sec)	121.69	128.58	112.47	117.35	146.76	117.36	130.17	116.41
Avg. HRR (300 sec)	85.05	89.21	69.82	91.46	114.44	79.17	85.73	75.52
Total HRR (MJ/ sq. m)	25.9	26.9	21.1	27.8	34.5	23.9	25.9	22.2
Smoke Avg. Spec. Ext. Area (sq. m/kg)	909.4	1053.3	763.9	855.4	726.1	905.7	765.9	1052.3
Glass Transition Temperature (C)	90	90	80	95	90	100	95	85

To summarize these results, API has found that with the use of phosphorous containing compounds, used in the textile industry, mechanical and physical properties of the epoxy resin is not significantly changed while providing substantial benefits for reducing fire and smoke values. The values for Total HRR, Avg HRR, and smoke are a significant improvement over what has been observed by API in past research and are almost as good as reported literature values for brominated vinyl esters.(1)

With the limited testing, it was determined that the phosphorous based reactive modifier showed little difference in heat release rates but made a significant difference in smoke. The epoxy functional phosphorous material provided lower smoke values than the hydroxyl functional material. Changing the base epoxy resin made a significant difference in heat release rates with more aromatic epoxy resin being better. The effect of silicone material in the formulation was small, but the amine functional polysiloxane curing agent proved to be much better reducing smoke than the pre-adducted silicone material.

With the results generated from this research, API formulated VaRTM capable resins using much more of the phosphorous based materials in higher crosslink density and more rigid epoxies. API selected epoxy resins having more aromatic structures in the backbone such as epoxy novolacs. This is due to the lower heat release rates observed when DGEBA was used with DGEBA (resin 6) instead of DGA (resin 1). It is assumed that the higher heat release rates observed when DGA was used in the formulation was due to the pendent phenyl ring that is not directly in the backbone. Due to the excellent processing characteristics and thermal properties, MXDA was used as the curing agent for the reformulated resins. Three new VARTM resins were developed as shown in Table 3.

Table 3. Reformulated VARTM Resin Formulations

Resin Formulation	9	10	11
Epoxy Novolac	40	80	
Epoxy DGA	40		
Epoxy MXDAE			80
Epoxy func. phosphorous compound	20	20	20
Aluminum trihydrate	10	10	10
MXDA	24	22	30

DGA-diglycidyl aniline

MXDAE-epoxidized metaxylenediamine

MXDA- metaxylenediamine

These three VaRTM resins were developed to compare the effects of FST properties of different types of epoxy resins in combination with a higher concentration of the phosphorous based modifier. Testing was performed at VTEC labs, using ASTM E1354- Cone Calorimeter Testing. All specimens had a thickness of 5.2 mm and were subjected to a heat flux of 50 kW. Results are summarized in the Table 4.

Table 4. Results of Cone Calorimeter Testing of VARTM Resins

Resin #	9	10	11
Time to Ignition (s)	80	78	84
Peak HRR (KW/sq. m)	192.91	170.26	215.86
Avg. HRR During Burning	95.75	71.58	82.96
Avg. HRR (180 sec)	120.13	95.62	101.53
Avg. HRR (300 sec)	76.6	62.03	62.22
Total HRR (MJ/ sq. m)	23.1	18.6	18.7
Smoke Avg. Spec. Ext. Area (sq. m/kg)	563.8	527.5	449.4
Glass Transition Temperature (C)	90	90	95

As shown in Table 4, resin formulation number 10 had the best balance of FST properties due to the more aromatic nature of using an all novolac resin when compared to an epoxy resin based on bisphenol-A and bisphenol-F resins, and epoxidized m-xylenediamine. The resin formulation 10 has similar cone calorimeter results as Derakane 510-A but with the added benefit of at least a 65 percent lower smoke value.

Summary

API has found that with the use of phosphorous containing compounds, used in the textile industry, substantial reduction in FST properties can be realized for VaRTM resins systems without loss in mechanical and physical properties. With using this new technology, API was able to developed an epoxy based resin system that exceeds the present state of the art epoxy VaRTM resin formulations. Collectively, as stated in the objective of this SBIR, API was able to develop a VaRTM processable resin that had equal cone calorimeter results as Derakane 510-A, but had at least a 65 % lower smoke value.

References:

Usman, S. Ness, J., and Blum, M. Fire Safety of Composites in the US Navy, Composites: Part A, vol 30, (1999) 707-713